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Vapor pressure and vapor fractionation of silicate melts of tektite composition

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Abstract—The total vapor pressure of Philippine tektite melts of approximately 70 per cent silica has been determined at temperatures ranging from 1500 to 2100°C. This pressure is 190 ± 40 mm Hg at 1500°C, 450 ± 50 mm at 1800°C and 850 ± 70 mm at 2100°C.

Determinations were made by visually observing the temperature at which bubbles began to form at a constant low ambient pressure. By varying the ambient pressure, a boiling point curve was constructed. This curve differs from the equilibrium vapor pressure curve due to surface tension effects. This difference was evaluated by determining the equilibrium bubble size in the melt and calculating the pressure due to surface tension, assuming the latter to be 380 dyn/cm.

The relative volatility from tektite melts of the oxides of Na, K, Fe, Al and Si has been determined as a function of temperature, total pressure and roughly, of oxygen fugacity. The volatility of SiO_2 is decreased and that of Na_2O and K_2O is increased in an oxygen-poor environment. Preliminary results indicate that volatilization at 2100°C under atmospheric pressure caused little or no change in the percentage Na_2O and K_2O. The ratio Fe^3/Fe^2 of the tektite is increased in ambient air at a pressure of 9×10^{-4} mm Hg ($= 10^{-6.5}$ atm O_2, partial pressure) at 2000°C. This suggests that tektites were formed either at lower oxygen pressures or that they are a product of incomplete oxidation of parent material with a still lower ferric–ferrous ratio.

INTRODUCTION

IN the aerodynamic analysis of tektites, ADAMS and HUFFAKER (1962) were forced to approximate the vapor pressure function for material of tektite composition. This approximation was based on the thermodynamic calculations of SCHICK (1960), and possible errors resulted in relatively great variability in the conclusions drawn from ablation analysis. It was hoped that pertinent experimental data could be obtained and applied.

The more accurate methods known as the Langmuir and Knudsen techniques were considered and discarded as being too costly in time and effort in view of the complex chemistry of tektites and the necessity, in these investigations, for data on the molecular weight of the species in the vapor and their accommodation coefficient. The "boiling point" method which was used and is described in this paper was thought, at first, to be too crude but worth an attempt since preliminary investigations were rather simple. The results of these preliminary studies were interesting and encouraging, so the study and the apparatus were enlarged as described here.

If one considers, or agrees to consider, that tektites have experienced thorough heating to high temperatures for moderate periods of time, it is conceivable that their bulk chemical composition has been modified by selective fractionation of vapor from the liquid phase. In this case, analysis of the bulk composition of tektites cannot be compared with trends of igneous or sedimentary differentiation.

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Vaporization differentiation trends are a function of temperature, pressure and oxygen pressure. Since earlier work on vaporization fractionation of tektite melts (FRIEDMAN, THORPE and SENFTLE, 1960; LOVERING, 1960) were all performed at atmospheric pressure and under conditions of heterogeneous temperature distribution, a study under controlled conditions was undertaken.

The purpose of the fractionation study was to enable extrapolation from tektite composition to the parent composition. While the results reported here are insufficient and too scattered to permit such an extrapolation, the study was rewarded by several unexpected results.

THEORY OF VAPOR PRESSURE DETERMINATIONS

Boiling of a liquid is achieved, theoretically, at the temperature at which the vapor pressure equals the ambient pressure. Thus, neglecting several other factors which will be discussed, it is possible to construct a vapor pressure curve by determining the boiling temperature as a function of ambient pressure.

Three factors, however, compromise this theoretical relationship:

1. The viscosity of the melt may prohibit the formation of bubbles; the melt "steaming" off the surface faster than bubbles can form. Using the function for viscosity determined by CHAPMAN and LARSON (1963) which indicates a viscosity for tektite melts of approximately 500 poises at 1800°C, a pressure differential of 5 dyn/cm^2 is found to be sufficient to cause a bubble to expand 0·1 mm/sec. Since bubbles growing at rates less than this could be observed and were considered evidence of boiling, the effect of viscosity is considered negligible.

2. Another force exerted on the point at which a bubble forms during boiling is the weight of the overlying mass of melt. This factor might be an appreciable portion of the total pressure on this point when the ambient pressure is reduced to a few millimeters of mercury, or when the column of liquid above the point is quite high. Since the melts studied were no greater than two millimeters thick, the weight of the overlying material (assuming a specific gravity of 2·5 g/cm^3) was no greater than the equivalent of 0·4 mm Hg pressure.

3. The final factor in the divergence of boiling point from vapor pressure determinations is the surface tension. This factor, σ, is related to the pressure which it exerts on a point in the melt P_s, by the relationship:

$$P_s = \frac{2\sigma}{r}$$

in which r is the radius of a bubble in the melt. The pressure due to surface tension will cause bubbles with a radius less than a critical value to diminish in size while those with greater radii will expand. Assuming a value of 380 dyn/cm based on an experimental determination on a tektite by CHAPMAN (personal communication, 1963) for the surface tension (variations of 50 dyn/cm in this figure yield results which are still well within the stated limits of error) and a value of 0·005 cm for the bubble radius, it was calculated that corrections for this factor would be about 100 mm Hg—an appreciable error in the boiling point determinations. The error was obviated by the experimental determination of the critical bubble size and

calculation of P_s which will be discussed. Although the surface tension will vary as a function of temperature, this factor was neglected since this variation would be a second order correction in the vapor pressure determination and thus unwarranted within the limits of error.

Apparatus

Preliminary studies were carried out in a vacuum coating unit consisting of a roughing pump, four-inch oil diffusion pump, steel baseplate and 18 in. diameter glass belljar. Initial attempts to heat the sample in tungsten crucibles by resistance heating of a small furnace of tungsten wire failed because conductive transfer of heat in a vacuum is quite low. Sample temperatures never exceeded 600°C although the windings were at 2600°C and only $\frac{1}{8}$ in. away. Final design of this apparatus utilized a single tungsten strip as a sample container and heating element, three inches long, 0·004 in. thick and $\frac{1}{2}$ in. wide. This strip was necked down to $\frac{3}{8}$ in. for the central $\frac{3}{4}$ in. to produce a hot spot and eliminate excessive heating of the electrodes which were made of steel. The sample was contained in a $\frac{1}{8}$ in. deep depression in the center of the strip which was formed by pressing the strip in a mold at about 400°C. Discussion of this apparatus is limited here, however, since it was used only for preliminary runs and one run discussed in this paper.

All other runs reported here were made in an apparatus, illustrated in Fig. 1, which permitted the use of iridium as a sample container. While the use of iridium was limited to temperatures below 2350°C, it has the advantage of being less reactive than tungsten. Since the preliminary results indicated that the vapor pressures of tektites were greater than originally thought, it proved possible to reach sufficiently high temperatures using iridium crucibles heated with a 10 kW induction heater.

Iridium crucibles were fabricated from 0·001 in. thick sheet by simply pressing a $\frac{1}{4}$ in. diameter ball bearing into the center of a $\frac{1}{2}$ in. diameter iridium disk (previously annealed at ~1800°C) supported on a semi-hard rubber pad. Many of the crucibles were made from 0·004 in. thick sheet and these had to be annealed, pressed with a one-inch ball bearing; annealed, pressed with a $\frac{3}{4}$ in. ball bearing and so on, continually decreasing the size of the sphere until a shallow dish was formed. The end-product was a dish a little over $\frac{1}{4}$ in. in diameter and about $\frac{1}{8}$ in. deep in the center. The iridium dishes were re-used after cleaning in HF after each vapor pressure determination. Those used in the fractionation studies had to be destroyed during sample removal.

The crucibles were placed on zirconia powder which was contained in the flared end of a silica-glass tube. This tube and the crucible were then enclosed in a one-inch diameter silica glass tube about 12 in. long which was sealed on one end by an optically smooth glass disk. The lower end of the one-inch tube was then sealed with wax to the vacuum system which consisted of a roughing pump and two-inch diameter air-cooled oil diffusion pump.

Continuous visual observation of the sample and temperature measurement was made with a *Pyro* optical pyrometer which was fitted with a close-up lens. The sample in the vertical tube was observed with the horizontal optical pyrometer through a 45° prism.

As indicated in a previous section, it became necessary to measure the size of the

bubbles produced in the boiling process. A semi-transparent 45° prism was therefore substituted for the simple prism normally used and the image of a graduated reticle was superimposed on the image of the sample in the pyrometer. The brightness of the sample was so much greater than that obtainable for the reticle that an intermediate standard, the V-shaped filament of the pyrometer, was calibrated (in terms of its

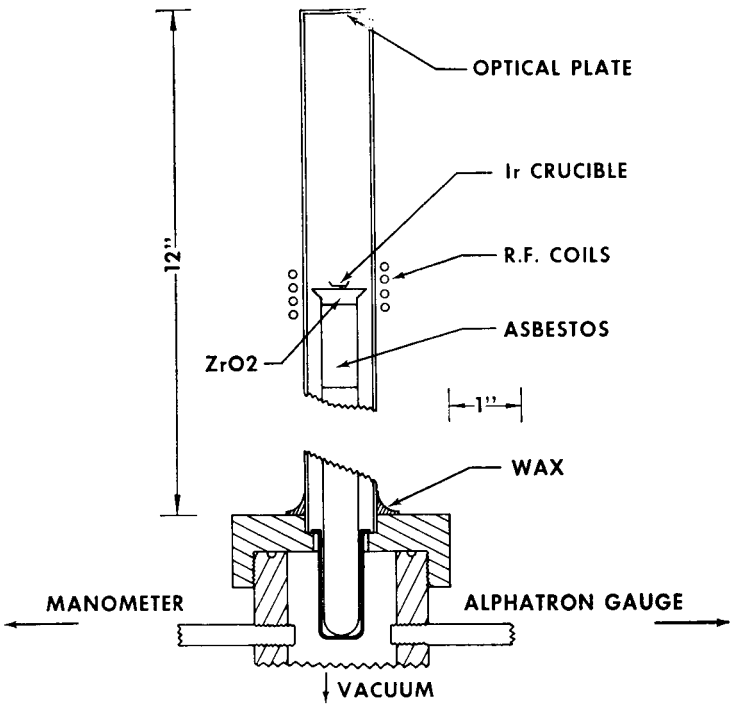

Fig. 1. Diagram of the apparatus in which samples were heated in iridium crucibles by an induction furnace.

apparent size when superimposed on the sample image) using the reticle as primary standard. The diameters of the bubbles varied between one and three wire diameters which corresponded to about 0·003 cm.

CALIBRATION

In the measurement of pressure, most determinations were made using a mercury manometer considered to be accurate to within 2 mm mercury. Pressure measurements below 10 mm were made with an alphatron ionization gauge which is considered accurate to within 10 per cent.

The entire temperature measurement system was calibrated at one time, based on the determination of the apparent melting temperatures of oxides with known melting points (this calibration curve is shown in Fig. 2). Since the composition and therefore the emissivity of the sample material was a variable in the study, it was

decided to calibrate the temperature of the sample based on the brightness temperature of the rim of the crucibles. Variations in the pyrometer, emissivity corrections for the particular shape of iridium crucible and absorption corrections for the prism and the viewing disk in the silica glass tube were all simultaneously calibrated and this system was kept constant throughout the study.

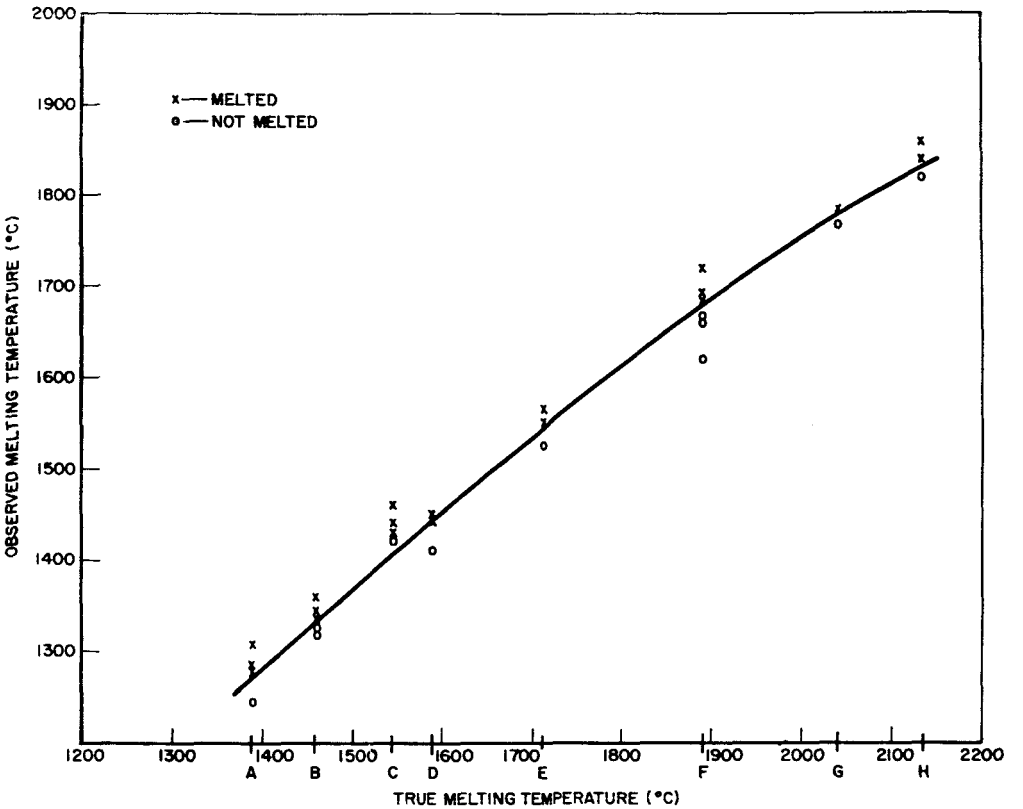

Fig. 2. Temperature calibration curve showing true vs. apparent melting temperatures for the following oxides: A—$CaMgSi_2O_6$; B—$CaMgSiO_4$; C—$CaSiO_3$; D—$Ca_2Al_2SiO_7$; E—SiO_2; F—Mg_2SiO_4; G—Al_2O_3; H—$MgAl_2O_4$. Circles indicate that the oxide did not melt while crosses indicate melting.

There are several indications as to the accuracy of this calibration. There was little reaction between the oxide and the iridium crucible; because calibration was carried out at atmospheric pressure, there was probably little dissociation before melting and therefore no lowering of the true melting points; the smoothness of the calibration curve indicates that the calibration is at least internally consistent.

Temperature differences of about 30° could be measured on an empty crucible at the temperatures at which runs were made. Greater variations, however, can be expected in and through non-circulating material contained in the crucible because of the low thermal inertia of the system. The significance of this fact is mitigated, however, by two factors. The material investigated is boiling, convecting and the material and thermal transfer tend to iron out the thermal gradient. More important,

however, is the fact that the sample will be hottest and will boil first where it is in contact with the crucible. Indeed, the calibrations were made under the same conditions, namely the determination of the melting points at the hottest point in the sample, i.e. near the crucible. Variation due to thermal gradient is thus compensated by the method of calibration. It is believed that the temperatures were accurate to within 25°C.

RESULTS

Since it was not possible to obtain a large amount of analysed tektite material for the entire vaporization study, one rather large philippinite was used to obtain

Table 1. Analyses of materials used in vapor pressure determination (analysis by U.S. Geological Survey)

	Bediasite B-105 (Analysts, M. K. CARRON and F. CUTTITTA)	Bediasite 30775-77	Grey obsidian TM-2 (partial) From Xalataquillo, Mexico (Analyst, F. CUTTITTA)
SiO_2	73·36	80·17	72
Al_2O_3	16·04	11·19	13·8
Fe_2O_3	0·31	0·18	0·8
FeO	4·81	2·82	
CaO	0·61	0·56	0·6
MgO	0·75	0·37	0·1
MnO	0·03	0·04	0·08
BaO	0·06		
Na_2O	1·44	1·53	
K_2O	1·93	2·24	3·2
P_2O_5	0·03	0·03	
TiO_2	0·87	0·60	<0·2
H_2O^+	(51)		
H_2O^-	(51)		
Total	100·24	99·73	90·58

the vapor pressure curve. Both the refractive index (1·510 ± 0·005) and density (2·44 g/cm³) were determined for the specimen, and they agreed with each other according to curves presented by CHAO (1963). These values indicate a silica content of 70–72% by weight. Additional runs were made on two bediasites of extremely divergent compositions and on an obsidian sample which, after crushing, was dried at about 500°C for several days. Chemical analyses of these specimens appear in Table 1. The tektite material used in the investigation was prepared by dry grinding to a fine powder in an agate mortar.

In the determination of the boiling point, the powdered sample in the crucible under vacuum was gradually heated until it became fluid. Following this the temperature was slowly raised and recorded until boiling was observed. It was often possible to reverse the boiling process several times before fractional volatilization resulted in a significant increase in the boiling temperature. The critical bubble size and the pressure due to surface tension was determined in several steps: (1) the

Table 2

(a) Boiling point determinations

Pressure (mm Hg)	No boiling (°C)	Boiling (°C)
2·8	1420	1445
4·0	1320	1340
7·6	1440	1475
7·6	1455	1465
7·4	1465	1495
12·0	1350	1370
10·0	1455	1475
18·0	1340	1355
160·0	1460	1500
22·0	1435	1480
25·0	1455	1495
26·0	1445	1500
32·0	1425	1475
47·0	1495	1510
52·0	1455	1485
70·0	1455	1485
98·0	1475	1510
120·0	1510	1520
140·0	1600	1615
120·0	1620	1630
198·0	1590	1620
190·0	1665	1695
210·0	1715	1735
400·0	1805	1835
598·0	2015	2135

(b) Vapor pressure determinations corrected for surface tension

P (ambient) (mm Hg)	T(°C)	r(cm)	P (vapor) (mm Hg)
166	1485	0·008	238
80	1435	0·0075	156
110	1525	0·008	181
126	1560	0·007	208
145	1605	0·006	240
318	1575	0·015	356
300	1725	0·0075	376
380	1775	0·006	475
500	1890	0·005	610
312	1620	0·006	412
760	2170	0·009	828

sample temperature was raised until bubbles were formed in the melt; (2) the temperature was then lowered and shrinking bubbles in the melt were sought; (3) the temperature was then raised a small amount (*ca.* 30°) to see whether the bubbles could be made to expand and contract in phase with the small rise and fall of temperature. When these events were observed (they were observed in approximately 50 per cent of the runs) the critical size, that is the size above which the

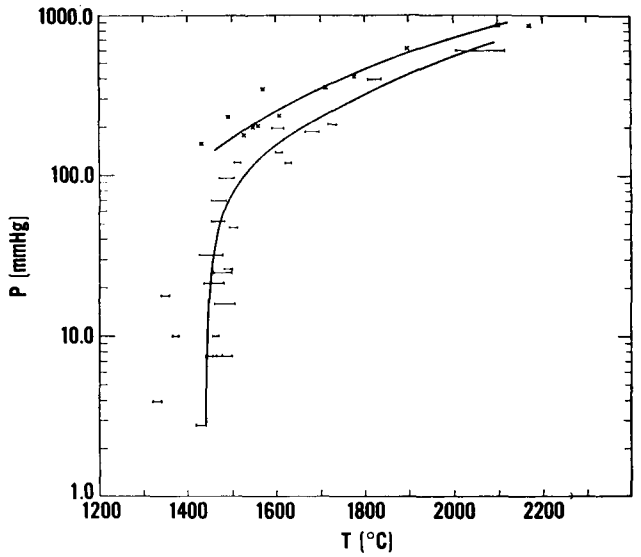

Fig. 3. Boiling point (lower) and critical bubble size (upper) curves for philippinite with 70–72% silica. The upper curve is considered to be the vapor pressure curve for the material. Brackets which determine the position of the lower curve indicate the boundary limits of observations, i.e. above which the melt was observed to boil and below which it did not boil.

bubbles seemed to grow and below which they seemed to contract, was determined with respect to the pyrometer filament. Using the expression previously described, the pressure due to surface tension was then computed and this value was added to the ambient pressure in order to obtain a closer value for the vapor pressure of the melt.

Data for the runs obtained by these methods appear in Table 2. The results are illustrated in Fig. 3. The lower curve in this figure is for the boiling point determination and does not take into account corrections for surface tension. At higher temperatures, it is relatively closer to the upper curve which takes into account surface tension and is based on the critical bubble size determinations. Brackets on the lower curve do not indicate limits of error but indicate the temperature limits of observation. That is, the higher temperature points on the brackets indicate those temperatures at which the samples were first observed to boil while the lower points indicate the highest temperatures at which the samples did not boil. The sharp drop in the lower boiling point curve is a result of the increased relative importance of the surface tension correction at lower pressures. Uncertainty of the vapor pressure

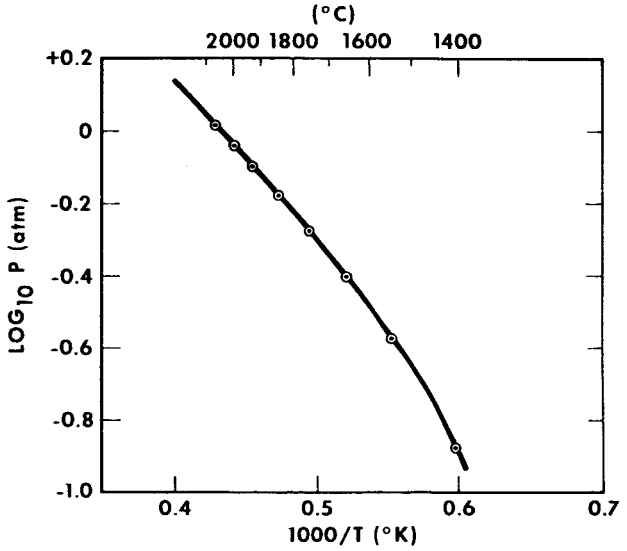

Fig. 4. The vapor pressure curve of Fig. 3 plotted as log P against reciprocal temperature.

values at the lowest temperatures is also increased by the possibility that the temperatures are below the liquidus temperatures for these silicic compositions.

The log of the vapor pressure is plotted against the reciprocal temperature in Fig. 4.

In Fig. 5, results of the runs on the bediasite and obsidian samples are superimposed on the curves presented for the philippinite sample. It appears that this method is unable to distinguish any differences in the vapor pressures of these materials and, within the limits of error, the results fall on the earlier curves. The

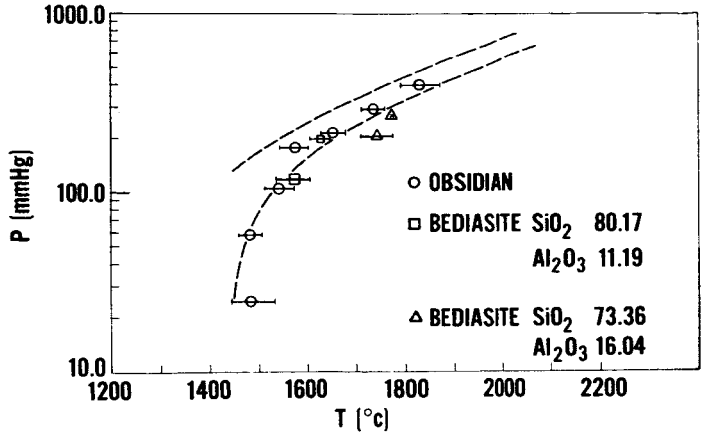

Fig. 5. Results of vapor pressure and boiling point determinations on two bediasites and an obsidian. For purposes of comparison, the curves of Fig. 3 are reproduced as dashed lines.

limits of error, however, are quite large, and significant differences, especially in terms of fractional volatilization, may still exist among these melts.

DISCUSSION OF VAPOR PRESSURE RESULTS

One important consideration in the interpretation of the results of the boiling point and equilibrium bubble size determinations is the possibility that these observed bubbles are caused by normally volatile constituents (H_2O, CO_2 etc.) dissolved in or adsorbed onto the grains of the glass. Several observations, however, mitigate against this possibility:

1. Tektites boil in spite of their exceptionally low content of normally volatile constituents.

2. The boiling points of tektites are, in some cases, higher than obsidian, which probably has a far greater content of normally volatile constituents.

3. One run was made at the suggestion of D. TILLES on a single sliver of philippinite ($\frac{3}{16}$ in. in diameter and about $\frac{1}{16}$ in. thick). At low pressure (1 mm Hg) this sample began to boil at a temperature between 1400 and 1500°C.

4. The rapid expansion over a very short temperature interval (see Fig. 2) cannot be ascribed to the PVT expansion of small bubbles in the melt due to rising temperature.

5. If, at constant pressure, the temperature is raised considerably above the boiling point, the melt will continue to boil until it is completely vaporized.

6. If, at constant pressure, the temperature is raised slightly above the boiling point, boiling will cease after a while, but resumes if the temperature is raised. The more volatile fraction of the melt is being distilled off.

7. Although a completely liquid melt forms at temperatures around 1500°C, initial boiling may take place at considerably higher temperatures.

An interpretation that the bubbles are caused by some dissociative reaction in the melt with consequent release of a volatile phase is, of course, possible. The observed boiling point curve would therefore be interpreted as a P–T dissociation curve but, thermodynamically, there is no distinction between this and a vapor pressure curve; the pressure necessary for reversing the dissociation being the vapor pressure of the substance.

VAPOR FRACTIONATION EXPERIMENTS

In all, six runs were made in which the change in chemical composition of tektite melts due to fractional volatilization were studied. Five of these runs were made in iridium crucibles and were heated with an induction furnace. One run was made in a tungsten crucible—heating element in a vacuum coating unit. The apparatus has been described in a preceding section. In a continuing study, an attempt will be made to precipitate the vapor in a cold trap and to study its structure and composition.

The accuracy stated for temperature and pressure determinations in the section on vapor pressure measurements also holds for the present investigation, even for the run in a tungsten container. Weight loss was determined by weighing samples before and after heating. Determinations on empty crucibles indicate a maximum

of one milligram weight loss which has little effect on the results. Small amounts of impurity in the zirconia substrate resulted, occasionally, in small specks of zirconia clinging to the iridium, but the total amount of such material was never greater than a milligram and thus had only a minor effect on the apparent weight loss since the amount of sample was always more than 100 mg. The residual in the chemical analyses can be attributed only partially to CaO and MgO.

Chemical Composition of Samples and Residua

Four tektite melts were made from portions of two previously analysed philippinites, Pp-163 and Pp-216 (Cuttitta and others, 1962). Each melt, weighing approximately 100 mg, was analysed for alkalis, total iron as Fe_2O_3, ferrous oxide, silica and alumina. The paucity of sample sizes permitted only single determinations of most of these constituents. The envelopes of iridium and tungsten containing the melts were peeled back and the melts transferred to a boron cabride mortar, ground, and sieved through 92 mesh bolting cloth in a plastic holder.

Approximately 10 mg of the ground samples were dissolved in perchloric and hydrofluoric acids. Alkalis were determined by the flame photometer on an aliquot of the solutions. On another aliquot total iron as Fe_2O_3 was determined spectrophotometrically with ortho-phenanthroline.

Ferrous oxide was determined in each of the samples on portions weighing from 8 to 10 mg using a semi-microvolumetric method (Wilson, 1960). These results were confirmed by another run of each sample using an improved technique (Carron, in press) of the same method.

Silica and alumina were determined spectrophotometrically on another 10 mg portion of each sample. The samples were fused with sodium hydroxide and dissolved in hydrochloric acid. Silica was determined on an aliquot of the solution by the molybdenum blue method (Shapiro and Brannock, 1958) and alumina by the color produced with alizarin red S (Shapiro and Brannock, 1958).

Accuracy of all of these determinations was monitored by simultaneously running samples of rock standards G-1, W-1 (Fleischer and Stevens, 1962) and a 1 + 1 composite sample of these.

Discussion of Vapor Fractionation Experiments

Chemical analyses of the starting materials and of the products of the runs are listed together with run conditions and other pertinent information in Table 3. The first four runs, $V_{1,2,3,4}$ were designed to illustrate fractionation under varied, but controlled, conditions. The last two, V_5 and V_6, were made to check the surprising results obtained for the relative volatilization of the alkalis.

A discrepancy in the vapor fractionation method is implicit in the summation of the analyses of Table 3. These sums show a slightly greater decrease in the percentages of the constituents in the residual fraction than is consistent with the total weight loss. This discrepancy can be attributed to the sum of small errors in the analyses and to the inclusion of small amounts of crucible material with the material which was analysed. One or two milligrams of crucible material retained after sample separation could account for the apparent excess loss through volatilization and would mean that the analyses of the constituents of the residuum are lower by one or two per cent than the true amount.

Table 3. Chemical analyses of tektites before and after vaporization fractionation (analyst, M. K. CARRON)
(PP_{216} used for V_1 and V_2, PP_{163} used for V_3 and V_4; PP_0 used for V_5 and V_6)

	PP_{216}	V_1	V_2	PP_{163}	V_3	V_4	PP_0	V_5	V_6
Temp. (°C)	—	2010–2080	2060–2090	—	2050	1780	—	2050	2050
Press. (mm Hg)	—	$1{\cdot}5 \times 10^{-3}$	10^{-3}	—	760	9×10^{-4}	—	760	760
Crucible	—	W	Ir	—	Ir	Ir	—	Ir	Ir
Time (min)	—	8	5	—	8	30	—	4	20
Wt.% lost	—	15·2	22	—	9·2	2·5	—	6·6	27
SiO_2	70·56	70·4	67·3	71·68	68·5	71·00	—	—	—
Al_2O_3	13·6	14·1	16·9	12·41	11·9	12·4	—	—	—
K_2O	2·59	0·91	0·99	2·12	2·35	1·88	2·27	2·26	2·29
Na_2O	1·37	0·06	0·11	1·52	1·23	0·60	1·29	1·31	1·32
FeO	4·84	4·84	{2·99* / 3·14	4·68	2·99	4·33	—	—	—
Fe_2O_3	0·21	—	{0·59 / 0·42	0·30	2·08	0·73	—	—	—
Total	93·17	90·31	88·82	92·71	89·05	90·94			
Fe_2O_3/FeO	0·0435	—	{0·198– / 0·132	0·0641	0·70	0·168	—	—	—

* Braces indicate replicate analyses.

The results of the fractionation experiments are illustrated in Fig. 6. If the loss of a constituent were a function only of the amount in the melt, the log of the constituent in the residuum would be a linear function of the total weight loss. The plots of Fig. 6 assume that this relationship obtains. The loss of a constituent, however, is also a function of the other components of the melt, resulting in deviations from linearity of the curves. Figure 6 assumes that a linear relationship obtains, at least to a first approximation. The arrows in Fig. 6 indicate the weight loss of each sample.

The conditions of runs V_1, V_2 and V_3 represent a constant and substantial increase in oxygen fugacity. In the case of V_1, this factor must be extremely low since the tungsten crucible must soak up almost all oxygen as it becomes available. If it is assumed that the mole fraction of oxygen in the atmosphere in the case of V_2 was the same as that in air, the partial pressure was approximately $2{\cdot}8 \times 10^{-7}$ atmospheres. In the case of V_3, the partial pressure of oxygen must have been 0·21 atmospheres. Run V_4 is not highly significant due to the low vaporization loss, which makes the analytical errors more important.

Suggestions that the relative volatility of silica from tektite melts would be increased under conditions of extremely low oxygen pressure (due to increased loss of SiO) are contradicted by the evidence of runs V_1, V_2 and V_3. Indeed, the data show that the relative volatility of silica is increased at higher oxygen pressures. It is interesting to note that the percentage of silica decreases under all but the most reducing conditions.

The results on alkali volatilization are interesting and somewhat surprising. The relative volatility of Na_2O and K_2O increases with decreasing oxygen fugacity and, in fact, there is no significant relative loss of alkalis in runs made at atmospheric

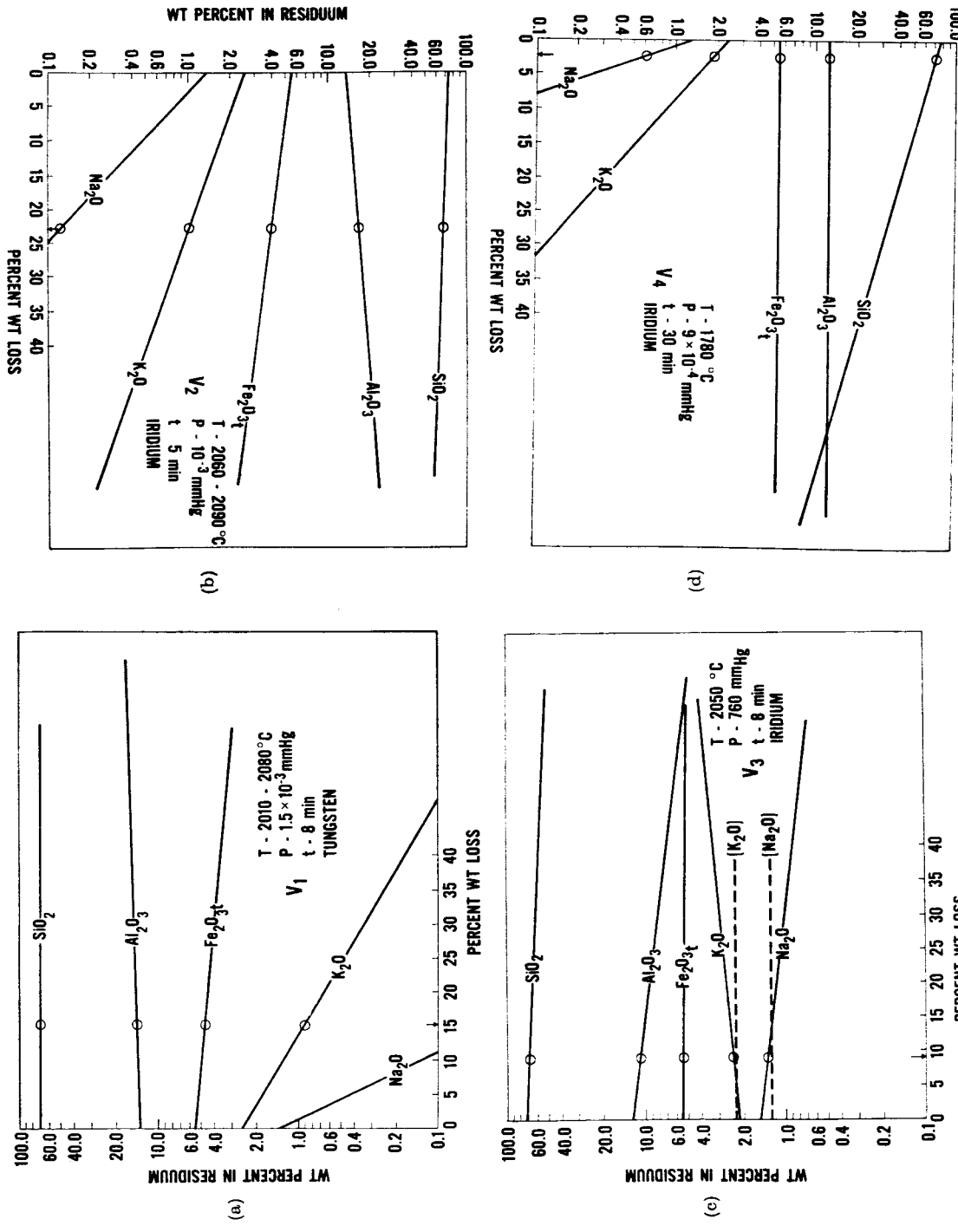

Fig. 6. Results of vapor fractionation experiments. Arrows at the abcissae indicates total weight losses. Results of additional runs to check alkali loss, V_5 and V_6 are shown in C as dashed lines. Since neither run showed any change in soda or potash content (although total weight loss was 6·6 and 27% respectively), results for the two runs are colinear. In all cases, total iron is calculated and plotted as Fe_2O_3.

pressure (P_{O_2} = 0·21 atm). Runs V_5 and V_6 were made to check this point and, as illustrated in Fig. 6(c), no change in composition was detected in either run. This data is in agreement with recent analyses of australite flanges and cores which indicate no constant relationship between the alkali contents of flange-core pairs (F. CUTTITTA, personal communication). The lack of fractionation of the alkalis under these conditions suggests that the alkali percentage was reduced to the present value by fractional volatilization and has achieved an equilibrium distribution

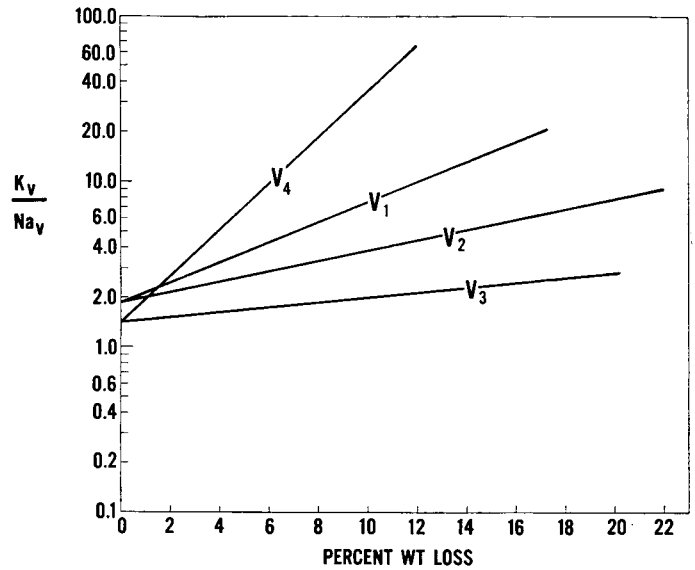

Fig. 7. The ratio of K_2O to Na_2O in the run products. The ratio increases constantly with increasing oxygen fugacity.

between melt and vapor at atmospheric pressure. This, of course, is only an approximate relationship since the vaporization experiments show that the bulk composition of the melt does, indeed, change even at atmospheric pressure and this, at least, necessitates a change in the mole fraction of alkalis in the melt in order to maintain the observed constant weight fraction. On the other hand, it is probably significant that the constituents generally considered to be most volatile are, under certain conditions, not depleted in the melt.

The ratio of K_2O and Na_2O also shows a constant relationship with P_{O_2} as shown in Fig. 7. This figure indicates that the value K_2O/Na_2O decreases with increasing oxygen pressure.

The values for the ratio Fe_2O_3/FeO shown in Table 3 indicate that in all cases (except the extreme reducing conditions of V_1) the ratio increased. Consideration of these data must place some limitations on the theories of tektite formation. If a terrestrial starting material is proposed, it is difficult to hypothesize a ferric–ferrous ratio lower than that found in tektites. Removal of oxygen into a rarified atmosphere is also questionable since the conditions of V_2 were at approximately 10^{-6} atm and the material was nevertheless oxidized. Reduction of the parent

tektite material by reaction with a metallic meteorite faces the objection of the high chromium to nickel ratio of tektites. Two possibilities are open to explain the ferric–ferrous ratios in the light of the experimental data. Most obvious is that tektites were formed under reducing conditions similar to those of V_1, perhaps at the lunar surface. An alternative is that the parent material was, indeed, oxidized but initially had a lower ferric–ferrous ratio than observed in tektites. It may be that the rocks of the Moon, having experienced a one-way degassing process, have, at least near the surface, a deficiency of oxygen. This might even result in the abundance of species such as SiO at the lunar surface. It may be therefore, that such material was oxidized in the terrestrial atmosphere but that it did not have enough time to achieve equilibrium.

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